

Self-assembly of Ag-phosphotungstic acid composite nanoparticles on a modified ITO electrode for the electrochemical detection of 4-chlorophenol

Yuanyuan Zhu · Manmei Wu · Shantang Liu

Received: 16 May 2013 / Accepted: 13 July 2013 / Published online: 24 July 2013
© Springer Science+Business Media Dordrecht 2013

Abstract Ag-phosphotungstic acid composite nanoparticles (Ag-PTA NPs) were synthesized by the reduction of silver nitrate with UV-irradiation in a PTA solution, followed by the assembly of the nanoparticles onto chitosan (CTS)-modified ITO-glass to be used for the electrochemical detection of 4-chlorophenol (4-CP). This modified electrode considerably increased the oxidation signals of 4-CP, which demonstrated its high electrocatalytic activity. The oxidation of 4-CP on the modified electrode is a reversible process controlled by surface absorption. The results of differential pulse voltammetry (DPV) showed that the peak current is linear with the 4-CP concentration in the range from 1 μM to 0.4 mM, with a correlation coefficient of 0.999, a response sensitivity of 0.1247 $\mu\text{A}/\mu\text{M}$, and a detection limit of 0.34 μM ($S/N = 3$). These results, combined with the electrode's good reproducibility, stability, and anti-interference performance, certainly make the Ag-PTA/CTS/ITO electrode a potential electrochemical sensor for the detection of chlorophenols.

Keywords Sensors · Silver · Nanoparticles · Electrochemical catalysis · Chlorophenols

1 Introduction

Chlorophenols (CPs), widely used for the production of dyes, drugs, pesticides, and fungicides, are notorious for

their toxicity as carcinogens and their environmental persistence character [1]. As a major class of organic pollutants, they contaminate the ecosystem and easily accumulate in the food chain. Thus, CPs are listed as priority pollutants by the U.S. Environmental Protection Agency (EPA, Toxic Substance Control Act, 1979). Consequently, the severe toxicity of CPs requires the development of a simple, sensitive, and reliable determination method. Several methods for the monitoring of CPs, such as high performance liquid chromatography (HPLC), gas-chromatography (GC), and biosensors, have been reported [2, 3]. Although these traditional methods possess excellent selectivity and high sensitivity, they require expensive instruments and often require a complex sample treatment and a long analysis time, which prevents their extensive application in the detection of CPs [4, 5]. In contrast, the electrochemical method is superior because of its low power consumption, inexpensive equipment, fast response, easy operation, and online detection. Thus, various electrochemical methods based on different chemically modified electrodes have been obtaining increasing attention in environmental monitoring [6, 7].

Nanoparticle composited films, particularly those with metal centers, deposited on electrode surfaces have attracted a wide scope of investigations due to their potential applications in various fields such as molecular electronics, photonics, electrocatalyst, corrosion protection, and chemical sensors [8, 9]. Nanosilver, one of the popular metal nanomaterials, has several advantages over other nanomaterials, such as its small size, large surface area, high surface activity and excellent catalytic performance, and has been assembled on electrodes to be used as electrocatalysts for various reactions [10–12]. Phosphotungstic acid (PTA), a solid polyoxometalate (PO_xM),

Y. Zhu · M. Wu · S. Liu (✉)

Key Laboratory for Green Chemical Process of Education Ministry, School of Chemical Engineering & Pharmacy, Wuhan Institute of Technology, 693 Xiongchu Road, Wuhan 430073, People's Republic of China
e-mail: stliu1@gmail.com

is usually applied for use as a catalyst or mediator because of its electron versatility and superior electroactivity [13–15]. In the Ag-PTA composite system, the combination of the Ag nanoparticle and PTA will generate synergistic effects and present some outstanding properties, which could make it an electrocatalyst with high activity. However, to the best of our knowledge, there have been no reports about an Ag-PTA-modified electrode being used for the detection of CPs. In addition, it is well known that the PO_xM undergoes a stepwise multi-electron redox process without enduring a structural change. It can participate in the catalytic redox process as an electron relay, and can be reduced electrolytically or photochemically [19]. It had been reported that the photolysis method with near-visible and UV-light can lead to the formation of metal nanoparticles, through a process in which PO_xM serves as photocatalysts, reducing reagents, and stabilizers [20]. PTA, as one of the PO_xM , is a switchable reducing agent that could easily be activated by a UV stimulus [19]. In this paper, the composite nanoparticles (NPs) of Ag-PTA are synthesized by the reduction of silver nitrate with UV-irradiation in a PTA solution.

The chitosan (CTS) has plenty of free primary amino groups and hydroxyl groups, whose protonated amino groups are positively charged under weakly acidic conditions, which make it possible to electrostatic self-assembly with the negated Ag-PTA composite nanoparticles. In our experiments, Ag-PTA composite nanoparticles were difficultly assembled on the bare ITO substrate, so we firstly modified the ITO with the positive CTS, which has advantages of semirigid macromolecule backbone, excellent film forming ability, and non-toxic. Then the Ag-PTA composite nanoparticles are assembled onto the CTS-modified ITO glass to obtain the Ag-PTA/CTS/ITO modified electrode. We used 4-CP as the CPs delegate. The conductivity and electrocatalytic activity of the Ag-PTA/CTS/ITO were studied by cyclic voltammetry (CV) in $\text{K}_3\text{Fe}(\text{CN})_6$ and 4-CP solutions, respectively. The results of the cyclic voltammetry (CV) in $\text{K}_3\text{Fe}(\text{CN})_6$ and 4-CP solutions showed that the obtained electrodes have good conductivity and high electrocatalytic activity. And also the synergistic effects might play a role in its superior performance. The linearity range and detection limit of 4-CP on the modified electrode were characterized by differential pulse voltammetry (DPV). A fast response to 4-CP was found with the Ag-PTA/CTS/ITO electrode, and its detection limit of $0.34\text{ }\mu\text{M}$ ($S/N = 3$) is lower than those of some reported utilizing a different type of nanoparticle [16, 17]. This research work is helpful in the development of electrochemical sensors for the detection of 4-CP with high-performance.

2 Experiments

2.1 Preparation of the modified electrode

2.1.1 Preparation of the colloidal solution of Ag-PTA composite NPs

The colloidal solution of Ag-PTA composite NPs was obtained by the reduction of silver nitrate under UV-irradiation in the presence of PTA [18]. Isopropanol (4 mL) was added to the mixture of 20 mL of 1 mM PTA solution and 20 mL of 1 mM silver nitrate solution with continuous stirring. Then, the mixture was irradiated by UV-light for 20 h after being ultrasonically degassed for 30 min. The solution was found to change from colorless to clear orange-yellow gradually, indicating the formation of the Ag-PTA composite NPs [18]. This colloidal solution was extremely stable and had no precipitation phenomenon after 4 months, illustrating that the PTA is bundled to the Ag NPs surface and stabilizes the Ag NPs electrostatically and stereochemically [19, 20].

2.1.2 Assembly of Ag-PTA NPs on the ITO-glass

The ITO-glass was ultrasonicated for 10 min in each of the following solvents: acetone, ethanol, and water. The ITO-glass was then rinsed with deionized water and dried by nitrogen purging. The CTS (BR, the degree of deacetylation was 80.0–95.0 %) was dissolved in 2 % acetic acid solution at a concentration of 2 mg/mL, and the solution was filtered by one-off pinhead strainer for subsequent use. The cleaned ITO-glass was immersed into the 2 mg/mL positive CTS solution for 1 h, washed with 2 % acetic acid and dried by nitrogen purging to obtain the positively modified ITO electrode. Then, the ITO electrode was dipped into the as-prepared Ag-PTA complex colloidal solution for 24 h (the optimal time for the reaction was obtained from multiple experiments). Finally, the ITO electrode was rinsed with deionized water and blown dry with nitrogen.

2.2 Electrochemical measurement

The electrocatalytic activity of the Ag-PTA/CTS/ITO electrode toward 4-CP was tested through CV and DPV. The applied parameters of DPV are as follows: a scan rate of 50 mV s^{-1} , a pulse modification of 50 mV in amplitude, and 50 ms in duration at intervals of 200 ms. To avoid instability in the measurements, the Ag-PTA/CTS/ITO electrode was first scanned 5 times in the buffer solution of 0.1 M $\text{Na}_2\text{HPO}_4\text{--NaH}_2\text{PO}_4$ (PBS). The electrolyte solutions were obtained by adding various quantities of 4-CP

stock solution to 10 mL of PBS with a pH = 6.7 under stirring, and then they were purged with high purity nitrogen for 30 min before each measurement. Electrochemical measurements were performed at room temperature (25 ± 1 °C) with mild magnetic stirring throughout the entire process.

2.3 Reagents and apparatus

CTS, PTA, silver nitrate, and 4-CP were purchased from Sinopharm Chemical Reagent Co. Ltd. Sodium phosphate buffer (PBS, pH = 6.7) was purchased from Hengxing Chemical Preparation Co. Ltd. All chemicals, except the CTS, were of analytical grade and were used as received without further purification. ITO-glass was obtained from CSG Holding Co. Ltd (10 Ω /square, size of 2 cm \times 0.6 cm \times 0.11 cm). Solutions were prepared from ultra-pure water with a resistivity over 18.0 M Ω cm that had been purified with a UPH-II-10 system (Youpu, China). All the glassware used was cleaned in a bath of freshly prepared 3:1 HCl/HNO₃, and was rinsed thoroughly with H₂O.

Surface morphologies of the Ag-PTA film on the ITO substrate were observed with an atomic force microscope (AFM, Multimode Nanoscope 3D, Veeco Instruments Inc, USA) in the tapping mode in air using standard Si₃N₄ cantilevers. UV–Vis absorption spectra of the Ag-PTA colloids and the Ag-PTA NPs attached to ITO substrates were recorded on UV-1800PC spectrophotometer (Mapada, China). The electrochemical performance of the modified electrode was studied by CV and DPV, which were performed on a CHI660 electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China) in a conventional three-electrode cell. A bare or modified ITO electrode with an exposed geometric area of ca. 0.5 cm² served as the working electrode. An Ag/AgCl (saturated KCl) electrode and a platinum wire are used as the reference and counter electrodes, respectively.

3 Results and discussion

3.1 Characterization of the Ag-PTA/CTS/ITO modified electrode

3.1.1 UV–Vis absorption spectra

Lines a and b of Fig. 1 show the UV–Vis absorption spectra of the Ag-PTA NPs colloidal solution and the Ag-PTA NPs film attached to an ITO substrate, respectively. The maximum absorption of the colloidal solution was at the wavelength of 436 nm (line a), which is the surface plasma resonance absorption of the silver NPs [21], indicating the successful formation of stable Ag-PTA

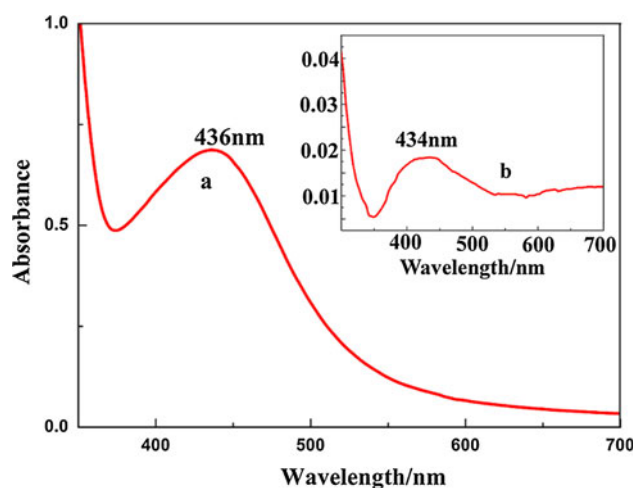


Fig. 1 UV–Vis absorption spectra of the Ag-PTA NPs colloidal solution (a) and the Ag-PTA NPs film attached to a CTS/ITO substrate (b)

composite NPs. Line b showed the largest absorption near 434 nm, showing a small shift compared with line a. The shift demonstrated that the Ag-PTA composite NPs were assembled on the positively charged ITO substrate. It has been noted that metal NPs absorption peaks usually have showed a red or blue shift when they were deposited from colloidal solutions to form films because of a difference in the dielectric properties around the NPs [22, 23], but the obtained Ag-PTA composite film showed nearly no shift of its absorption peak. This lack of shift could be attributed to the silver NPs being encapsulated by PTA, which resulted in negligible changes being generated in the dielectric environment of the silver NPs.

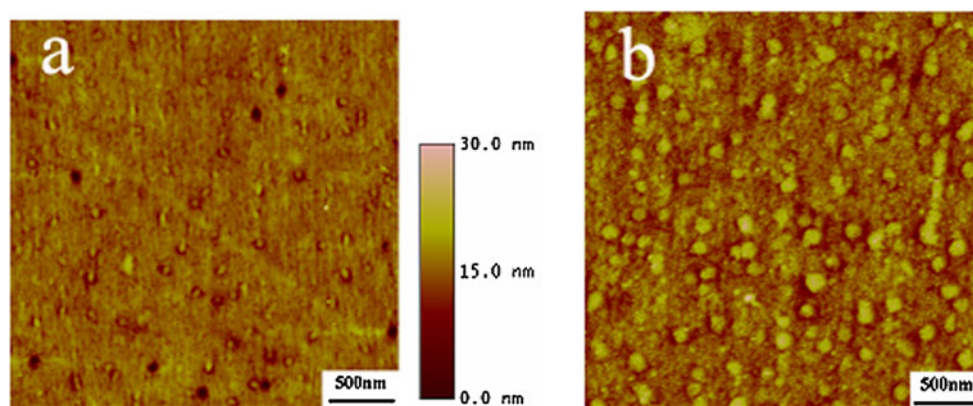
3.1.2 Surface morphology

The surface morphologies of the CTS/ITO electrode, both before and after modification by Ag-PTA NPs, were characterized by AFM. It can be seen from Fig. 2a that the CTS-modified ITO presents an amorphous morphology because of the polymer coverage. Figure 2b shows that the substrate was evenly covered by nanospheres with diameters of 50–75 nm. Combined with the results of the UV–Vis absorption spectra, it can be confirmed that the nanospheres were PTA-encapsulated silver NPs. Thus, the Ag-PTA/CTS/ITO modified electrode was successfully prepared.

3.1.3 Electrochemical behavior of the Ag-PTA/CTS/ITO electrode

[Fe(CN)₆]^{3-/4-}, which undergoes a reversible electrochemical reaction at various electrodes, is widely used as an electrochemical probe to investigate the films deposited on electrode surfaces [24]. Figure 3 shows the difference

Fig. 2 AFM images of the CTS modified ITO electrode (a) and the Ag-PTA/CTS/ITO electrode (b)



between the CV profiles of the CTS/ITO electrode (curve a) and the Ag-PTA/CTS/ITO modified electrode (curve b) in a 20 mM $\text{K}_3\text{Fe}(\text{CN})_6$ solution over the voltage range of 0–0.6 V. Curve a illustrates that $[\text{Fe}(\text{CN})_6^{3-/4-}]$ had a pair of redox peaks with a potential difference of $\Delta E_p = 182$ mV at the CTS/ITO electrode. Similarly, a perfectly symmetrical CV (curve b) was also found when $[\text{Fe}(\text{CN})_6^{3-/4-}]$ reacted at the Ag-PTA/CTS/ITO electrode, but when compared with curve a, curve b had a smaller potential difference of 160 mV and an obviously larger peak current. The redox peak potential difference ΔE_p , which is inversely proportional to the electron transfer rate [25], can be used for the electrochemical evaluation of the electrode conductivity. Clearly, the Ag-PTA/CTS/ITO electrode showed better conductivity than the CTS/ITO electrode. Because the redox peak current is proportional to the active reaction area under the same conditions, the larger current of curve b indicated that the assembly of Ag-PTA NPs on the CTS/ITO endowed the electrode surface with a higher electrochemical active area compared with the CTS modified electrode. This larger active area on the Ag-PTA/CTS/ITO electrode could result in more efficient heterogeneous catalytic reactions or electrochemical reactions [26]. Combined with the AFM images of Fig. 2, it can be concluded that the assembly of the Ag-PTA NPs on the CTS/ITO substrate, which gives rise to a rough surface, not only enhances the conductivity, but also provides a larger active reaction area.

3.2 Electrochemical detection of 4-CP

3.2.1 Electrochemical behavior of 4-CP on different electrodes

Before comparing the electrochemical behavior of 4-CP at the CTS/ITO and the Ag-PTA/CTS/ITO electrodes, the CVs of the two electrodes in the absence of 4-CP were investigated, as shown by curves a and c, respectively in Fig. 4. It can be observed that the two curves have similar

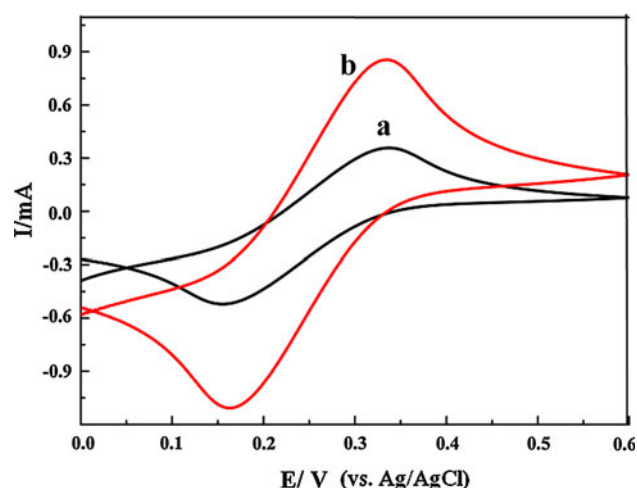


Fig. 3 CVs of the CTS/ITO electrode (a) and the Ag-PTA/CTS/ITO modified electrode (b) in 20 mM $\text{K}_3\text{Fe}(\text{CN})_6$ solution. Scan rate 50 mV/s

profiles: both do not have obvious corresponding peaks from direct electron transfer between the counter and work electrodes. Curves b and d illustrate the electrochemical reactions of 4-CP at the CTS/ITO and Ag-PTA/CTS/ITO electrodes in N_2 -saturated PBS at a pH = 6.7. The CV of 4-CP at the CTS/ITO electrode (curve b) showed a negligible redox peak. However, the CV of 4-CP at the Ag-PTA modified electrode exhibited a pair of well-behaved redox peaks at 0.95 and 0.4 V (vs. Ag/AgCl), indicating the oxidation of 4-CP on this electrode. Furthermore, the oxidation current of 4-CP at the Ag-PTA/CTS/ITO electrode is much larger than that at the CTS/ITO electrode, demonstrating that the Ag-PTA NPs films possess high electrocatalytic activity for the oxidation of 4-CP. From the reported reaction mechanism of 4-CP on nano Au film [27, 28], we can deduce the electrocatalysis principle of Ag-PTA NPs toward the 4-CP. First, H_2O molecules are adsorbed on the Ag-PTA NPs surface to form hydroxyl radicals (OH^\bullet) due to the electrooxidation of the Ag-PTA– H_2O sites, and then, the OH^\bullet causes the oxidation of 4-CP.

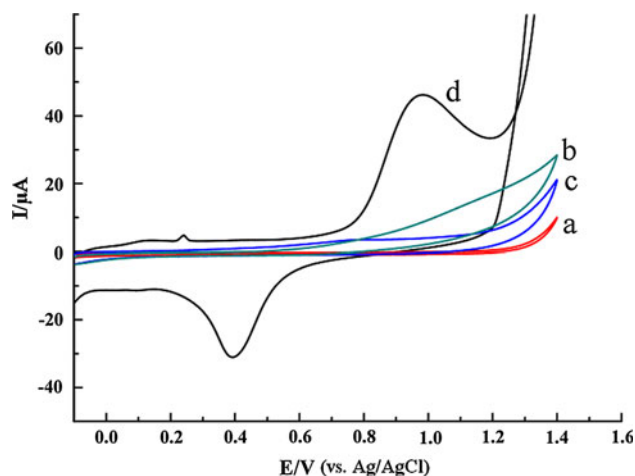


Fig. 4 CVs of CTS/ITO (a) and Ag-PTA/CTS/ITO (c) in the N_2 -saturated PBS (pH = 6.7); CVs of CTS/ITO (b) and Ag-PTA/CTS/ITO (d) in the above solution with 0.4 mM 4-CP. Scan rate 50 mV/s

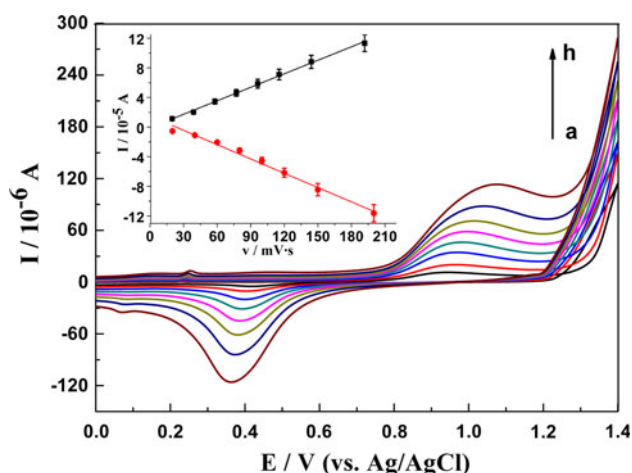


Fig. 5 CVs of the Ag-PTA/CTS/ITO electrode in 0.4 mM 4-CP solution with N_2 -saturated PBS (pH = 6.7) at different scan rates. The inset is the linear relationship of the redox peak current versus scan rate. a–h: 20, 40, 60, 80, 100, 120, 150, and 200 mV/s

3.2.2 Influence of the scan rate on the detection of 4-CP

It is common knowledge that the electrochemical behavior at the electrode/solution interface is directly dependent on the scan rate. Thus, the influence of the scan rate on the electrochemical reaction of 4-CP on the Ag-PTA/CTS/ITO electrode was also studied by CVs at scan rates ranging from 20 to 200 mV/s. As shown in Fig. 5, the anode and cathode peak currents are both increased with the enhancement of the scan rate, and the oxidation and reduction peak potentials shift positively and negatively, respectively. The good linear relationship between the redox peak current and the scan rate is represented in the inset of Fig. 5. The linear regression equations are as follows: I_p (10^{-5} A) = $-0.051 + 0.058 v$ (mV/s); I_p

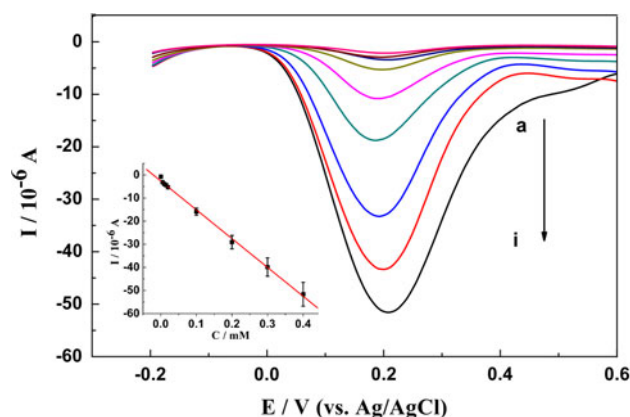


Fig. 6 DPV response of the Ag-PTA/CTS/ITO electrode to different 4-CP concentrations in N_2 -saturated PBS (pH = 6.7). The inset is the calibration plot of the linear relationship between the peak current and 4-CP concentration. a–i: 1×10^{-3} , 5×10^{-3} , 7.5×10^{-3} , 1.0×10^{-2} , 2.0×10^{-2} , 5.0×10^{-2} , 0.1, 0.2, 0.3, 0.4 mM. Scan rate 50 mV/s

(10^{-5} A) = $1.548 - 0.065 v$ (mV/s). The correlation coefficients are 0.998 and 0.993, respectively. In addition, the rate of the oxidation and reduction peak current was approximately equal to 1, which indicates that the electrocatalytic reaction of 4-CP on the Ag-PTA/CTS/ITO electrode is a reversible process controlled by surface absorption. To avoid an adverse effect on the detection of 4-CP by surface absorption, an accumulation process on the electrode surface prior to the test is essential. We found the optimal accumulation time to be 60 s through repeated experiments.

3.2.3 Linear range and detection limit

As described above, because the Ag-PTA/CTS/ITO electrode shows high electrocatalytic activity toward 4-CP, it can be a potential electrochemical sensor used to monitor the harmful CPs. The linear range and detection limit are two vital parameters for evaluating the usefulness of the prepared electrode. Figure 6 shows the DPV response of the Ag-PTA/CTS/ITO electrode with different 4-CP concentrations in N_2 -saturated PBS with a pH = 6.7 at a scan rate of 50 mV/s. As the concentration rose from 1 μ M to 0.4 mM, the peak currents increased from 2.6 to 52 μ A accordingly. Furthermore, the peak current is linear with the 4-CP concentration throughout the range of 1 μ M to 0.4 mM, as shown by the inset graph of Fig. 6. The linear regression equation of the peak current (I_p) versus the 4-CP concentration (C) is I_p (μ A) = $-2.612 - 0.125 C$ (μ mol/L), the correlation coefficient is 0.999, the detection limit is 0.34 μ M ($S/N = 3$), and the response sensitivity is 0.1247 μ A/ μ M.

The detection limit of the obtained Ag-PTA/CTS/ITO electrode is far lower than those reported for the expanded

Table 1 Response characteristics of different electrodes for detection of 4-CP

Type of composite electrode	Used technique	Sensitivity ($\mu\text{A}/\mu\text{M}$)	Correlation coefficient	Detection limit (μM)	Linear range (mM)
Expanded graphite–epoxy [16]	CV	0.45	0.996	20	0.08–1.0
Expanded graphite–Ag–zeolite–epoxy [17]	DPV	0.25	0.995	10	0.1–0.5
Nano Au/glassy carbon [28]	Typical steady-state response(I–t)	0.397	0.999	0.11	0.2–4.8
Ag-PTA/CTS/ITO	DPV	0.125	0.999	0.34	0.001–0.4

graphite–epoxy [16] and expanded graphite–Ag–zeolite–epoxy [17] electrodes, as shown in Table 1. Although the detection limit for the Ag-PTA/CTS/ITO electrode is a little larger than that of the nano Au/glassy carbon electrode [28], the optimization of the particle size and film thickness of the Ag-PTA NPs could improve the modified electrode performance. So future efforts will mainly be concentrated on the optimization of the Ag-PTA/CTS/ITO electrode to broaden the linear range, decrease the detection limit and enhance the sensitivity.

3.2.4 Reproducibility, stability, and anti-interference performance

The reproducibility and stability of the Ag-PTA/CTS/ITO electrode for the detection of 4-CP was also investigated. The repeatability of the current response of the Ag-PTA/CTS/ITO electrode to 0.4 mM 4-CP was evaluated in N_2 -saturated PBS with a pH = 6.7. Because the 4-CP absorbed on the electrode can influence the measurement, the electrode should be repeatedly scanned 15 times in the above 4-CP solutions before each test. The relative standard deviation (RSD) was 4.2 % for five successive assays, indicating the good repeatability of the Ag-PTA/CTS/ITO electrode. The excellent repeatability may be because the Ag-PTA NPs were attached uniformly and tightly onto the CTS-modified ITO surface.

The long-term stability of the modified electrode was also examined periodically during storage in a refrigerator at 4 °C. The electrode retained 92 % of its initial current response to the 0.4 mM 4-CP after 10 days and 80 % after 30 days. The excellent stability could be attributed to the strong interactions between the Ag-PTA NPs and the surface of the CTS-modified ITO and the firm immobilization of the PTA molecules on the silver NPs surface.

Finally, the influences of some interfering substances, particularly metal ions as well as organic and inorganic radical acid ions, on the practical monitoring of 4-CP were investigated. The experiments were conducted on the as-prepared Ag-PTA/CTS/ITO electrode in N_2 -saturated PBS containing 0.4 mM 4-CP with a pH = 6.7 in the presence of one of the following ions at a concentration of

40 mM: K^+ , Na^+ , Mg^{2+} , NO_3^- , H_2PO_4^- , HPO_4^{2-} , SO_4^{2-} , Ac^- , Cl^- , and Zn^{2+} . The response currents in the presence and absence of each interfering substance above-mentioned were compared, and this ratio was used as a criterion for the anti-interference performance of the electrode. These interfering substances did not have any observable interference. Moreover, glucose and ascorbic acid, which always exist when testing food, also had no influence on the oxidation peak current of 4-CP on the Ag-PTA/CTS/ITO electrode.

4 Conclusions

The synthesized Ag-PTA NPs were successfully deposited on the positive CTS-modified ITO electrode. The average size of the deposited Ag-PTA NPs was 50–75 nm, and they had a uniform distribution on the electrode. The Ag-PTA/CTS/ITO electrode not only showed high electrocatalytic activity toward the 4-CP, but also had fast response throughout the 4-CP concentration range of μM –mM. Moreover, the good repeatability, resistance to interference and stability of the electrode for detecting 4-CP were achieved. Therefore, using the Ag-PTA/CTS/ITO electrode to monitor the toxic CPs will be a simple and effective method, and future work will mainly be concentrated on the electrocatalytic mechanism toward 4-CP and other CPs, synergistic effect between Ag and PTA, optimization of the Ag-PTA/CTS/ITO electrode to improve its performance in practical applications.

Acknowledgments This study was supported by the National Natural Science Foundation of China (No. 21071113), the Natural Science Foundation of Hubei Province (No. 2011CDA049) and the International Cooperation Foundation of Hubei Province (No. 2012IHA00201).

References

1. Yamazaki S, Fujiwara Y, Yabuno S, Adachi K, Honda K (2012) Synthesis of porous platinum-ion-doped titanium dioxide and the photocatalytic degradation of 4-chlorophenol under visible light irradiation. *Appl Catal B* 121–122:148–153. doi:[10.1016/j.apcatb.2012.03.026](https://doi.org/10.1016/j.apcatb.2012.03.026)

2. Li JD, Zhao XL, Shi YL, Cai YQ, Mou SF, Jiang GB (2008) Mixed hemimicelles solid-phase extraction based on cetyltrimethylammonium bromide-coated nano-magnets Fe_3O_4 for the determination of chlorophenols in environmental water samples coupled with liquid chromatography/spectrophotometry detection. *J Chromatogr A* 1180:24–31. doi:[10.1016/j.chroma.2007.12.028](https://doi.org/10.1016/j.chroma.2007.12.028)
3. Sarafraz-Yazdi A, Mofazzeli F, Es'haghi Z (2009) A new high-speed hollow fibre liquid phase microextraction method using volatile organic solvent for determination of aromatic amines in environmental water samples prior to high-performance liquid chromatography. *Talanta* 79:472–478. doi:[10.1016/j.talanta.2009.04.015](https://doi.org/10.1016/j.talanta.2009.04.015)
4. Hanrahan G, Patil DG, Wang J (2004) Electrochemical sensors for environmental monitoring: design, development and applications. *J Environ Monit* 6:657–664. doi:[10.1039/B403975K](https://doi.org/10.1039/B403975K)
5. Wan CD, Zhang Y, Lin HG, Wu KB, Chen JW, Zhou YK (2009) Electrochemical determination of *p*-chlorophenol based on the surface enhancement effects of mesoporous TiO_2 -modified electrode. *J Electrochem Soc* 156:151–154. doi:[10.1149/1.3207946](https://doi.org/10.1149/1.3207946)
6. Inam R, Bilgin C (2013) Square wave voltammetric determination of methiocarb insecticide based on multiwall carbon nanotube paste electrode. *J Appl Electrochem* 43:425–432. doi:[10.1007/s10800-013-0526-5](https://doi.org/10.1007/s10800-013-0526-5)
7. Cañizares P, García-Gómez J, Sáez C, Rodrigo MA (2004) Electrochemical oxidation of several chlorophenols on diamond electrodes: part II. Influence of waste characteristics and operating conditions. *J Appl Electrochem* 34:87–94. doi:[10.1023/B:JACH.000005587.52946.66](https://doi.org/10.1023/B:JACH.000005587.52946.66)
8. Chauke VP, Chidawanyika W, Nyokong T (2011) The electrochemical behavior of gold nanoparticle–tantalum(V) phthalocyanine composites: applications towards the electroanalysis of bisphenol A. *Electroanalysis* 23:487–496. doi:[10.1002/elan.201000521](https://doi.org/10.1002/elan.201000521)
9. Quach AD, Crivat G, Tarr MA, Rosenzweig Z (2011) Gold nanoparticle-quantum dot-polystyrene microspheres as fluorescence resonance energy transfer probes for bioassays. *J Am Chem Soc* 133:2028–2030. doi:[10.1021/ja109348d](https://doi.org/10.1021/ja109348d)
10. Fenga PG, Stradiotto NR, Pividori MI (2011) Silver nanocomposite electrode modified with hexacyanoferrate. Preparation, characterization and electrochemical behaviour towards substituted anilines. *Electroanalysis* 23:1100–1106. doi:[10.1002/elan.201000651](https://doi.org/10.1002/elan.201000651)
11. Maheswari S, Sridhar P, Pitchumani S (2012) Carbon-supported silver as cathode electrocatalyst for alkaline polymer electrolyte membrane fuel cells. *Electrocatalysis* 3:13–21. doi:[10.1007/s12678-011-0071-0](https://doi.org/10.1007/s12678-011-0071-0)
12. Lee CL, Chiou HP, Syu CM, Wu CC (2010) Silver triangular nanoplates as electrocatalyst for oxygen reduction reaction. *Electrochem Commun* 12:1609–1613. doi:[10.1016/j.elecom.2010.09.007](https://doi.org/10.1016/j.elecom.2010.09.007)
13. Ramos-Fernandez EV, Pieters C, Linden B, Juan-Alcañiz J, Serra-Crespo P, Verhoeven MWGM, Niemantsverdriet H, Gascon J, Kapteijn F (2012) Highly dispersed platinum in metal organic framework $\text{NH}_2\text{-MIL-101(Al)}$ containing phosphotungstic acid—characterization and catalytic performance. *J Catal* 289:42–52. doi:[10.1016/j.jcat.2012.01.013](https://doi.org/10.1016/j.jcat.2012.01.013)
14. Shiju NR, Alberts AH, Khalid S, Brown DR, Rothenberg G (2011) Mesoporous silica with site-isolated amine and phosphotungstic acid groups: a solid catalyst with tunable antagonistic functions for one-pot tandem reactions. *Angew Chem* 123:9789–9793. doi:[10.1002/ange.201101449](https://doi.org/10.1002/ange.201101449)
15. Yuan JH, Jin XL, Li N, Chen JR, Miao JG, Zhang QX, Niu L, Song JX (2011) Large scale load of phosphotungstic acid on multiwalled carbon nanotubes with a grafted poly(4-vinylpyridine) linker. *Electrochim Acta* 56:10069–10076. doi:[10.1016/j.electacta.2011.08.093](https://doi.org/10.1016/j.electacta.2011.08.093)
16. Pop A, Manea F, Radovan C, Corb I, Burtica G, Malchev P, Picken S, Schoonman J (2008) Determination of 4-chlorophenol using two types of graphite-based composite electrodes. *Rev Roum Chim* 53:623–628
17. Pop A, Manea F, Radovan C, Malchev P, Bebeselea A, Proca C, Burtica G, Picken S, Schoonman J (2008) Amperometric detection of 4-chlorophenol on two types of expanded graphite based composite electrodes. *Electroanalysis* 20:2460–2466. doi:[10.1002/elan.200804348](https://doi.org/10.1002/elan.200804348)
18. Yang LB, Shen YH, Xie AJ, Zhang BC (2007) Facile size-controlled synthesis of silver nanoparticles in UV-irradiated tungstosilicic acid solution. *J Phys Chem C* 111:5300–5308. doi:[10.1021/jp067010s](https://doi.org/10.1021/jp067010s)
19. Pasricha R, Gupta S, Joshi AG, Bahadur N, Haranath D, Sood KN, Singh S (2012) Directed nanoparticle reduction on graphene. *Mater Today* 15:118–125. doi:[10.1016/S1369-7021\(12\)70047-0](https://doi.org/10.1016/S1369-7021(12)70047-0)
20. Troupis A, Hiskia A, Papaconstantinou E (2002) Synthesis of metal nanoparticles by using polyoxometalates as photocatalysts and stabilizers. *Angew Chem Int Ed* 41:1911–1914. doi:[10.1002/1521-3773](https://doi.org/10.1002/1521-3773)
21. Li Y, Wang CW, Liu WM, Li HL, Shigeaki Z, Ma S (2005) Plasma resonance absorption properties of the Ag–AAO nanoarray composite. *Acta Optica Sinica* 25:1649–1654
22. Ma YT, Di JW, Yan X, Zhao ML, Lu ZJ, Tu YF (2009) Direct electrodeposition of gold nanoparticles on indium tin oxide surface and its application. *Biosens Bioelectron* 24:1480–1483. doi:[10.1016/j.bios.2008.10.007](https://doi.org/10.1016/j.bios.2008.10.007)
23. Wang JW, Wang LP, Di JW, Tu YF (2009) Electrodeposition of gold nanoparticles on indium/tin oxide electrode for fabrication of a disposable hydrogen peroxide biosensor. *Talanta* 77:1454–1459. doi:[10.1016/j.talanta.2008.09.034](https://doi.org/10.1016/j.talanta.2008.09.034)
24. Zhang JD, Oyama M (2005) Gold nanoparticle-attached ITO as a biocompatible matrix for myoglobin immobilization: direct electrochemistry and catalysis to hydrogen peroxide. *J Electroanal Chem* 577:273. doi:[10.1016/j.jelechem.2004.12.005](https://doi.org/10.1016/j.jelechem.2004.12.005)
25. Harris JJ, Bruening ML (2000) Electrochemical and in situ ellipsometric investigation of the permeability and stability of layered polyelectrolyte films. *Langmuir* 16:2006–2013. doi:[10.1021/la990620h](https://doi.org/10.1021/la990620h)
26. Chen ZF, Zu YB (2007) Gold nanoparticle-modified ITO electrode for electrogenerated chemiluminescence: well-preserved transparency and highly enhanced activity. *Langmuir* 23:11387–11390. doi:[10.1021/la702417w](https://doi.org/10.1021/la702417w)
27. Peeters K, Wael KD, Bogaert D, Adriaens A (2008) The electrochemical detection of 4-chlorophenol at gold electrodes modified with different phthalocyanines. *Sens Actuators B* 128: 494–499. doi:[10.1016/j.snb.2007.07.039](https://doi.org/10.1016/j.snb.2007.07.039)
28. Qiu CC, Dong XQ, Ma HY, Hou SF, Yang J (2012) Electrochemical behavior and amperometric detection of 4-chlorophenol on nano-Au thin films modified glassy carbon electrode. *Electroanalysis* 24:1201–1206. doi:[10.1002/elan.201100662](https://doi.org/10.1002/elan.201100662)